Discoverer $PM_{2.5}$ Speciation Monitoring Program at Deadhorse

Shell Offshore Inc. (SOI)

Prudhoe Bay, Alaska

Quarterly Data Summary

January 1, 2012 – March 31, 2012

May 2012

SLR
global environmental solutions
AKreports@SLRconsulting.com
(907) 563-2137

QUARTERLY DATA SUMMARY

Prepared for:

Shell Offshore Inc.
3601 C Street, Suite 1334
Anchorage, AK 99503

This document has been prepared by SLR International Corp. The material and data in this report were prepared under the supervision and direction of the undersigned.

Brad Broker
SLR Project Manager

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The primary objective of the $PM_{2.5}$ Speciation Monitoring Program is to collect $PM_{2.5}$ chemical speciation data to comply with post construction ambient air quality monitoring requirements specified in permit condition S. of permit number R10OCS/PSD-AK-2010-01 for the Shell Offshore Inc. (SOI) Beaufort Sea Exploratory Drilling Program using the Noble Discoverer (Discoverer) drillship.

To accomplish this objective, $PM_{2.5}$ chemical speciation data, including sulfates, nitrates, organics, metals, sea salt and crustal matter will be collected at a location representative of the Beaufort Sea. The Deadhorse monitoring station has been determined by EPA to be representative of the Beaufort Sea. This report summarizes speciation sample results collected at the Deadhorse station for Quarter A of the monitoring program spanning from January 1, 2012 through March 31, 2012.

Table E-1 details Quality Assurance Project Plan (QAPP) variations documented for this project during the monitoring period. The Discoverer $PM_{2.5}$ Speciation Monitoring Program QAPP was submitted to the USEPA Region 10 in January, 2012, and approval is pending.

Table E-2 provides a summary of the project data recovery and data completeness.

Table E-1. QAPP Variation Table

Item / Procedure	Summary of QAPP Variation	Reason for making the variation
During the monitoring period, there were no variations from the approved procedures and criteria specified in the Discoverer $PM_{2.5}$ Speciation Monitoring Program Quality Assurance Project Plan (QAPP).		

Table E-2. Data Recovery and Data Completeness

Period	Planned Sample Events [1]	Actual Sample Events [2]	Valid $PM_{2.5}$ Mass Samples	Recovery Rate (%) [3]	Valid Nitrate (NO_3) Samples	Valid Sulfate (SO_4) Samples	Valid Organic Carbon (OC) Samples	Valid Elemental Carbon (EC) Samples	Data Completeness (%) [4]
January 2012	1	1	0	0	0	0	0	0	0
February 2012	5	5	3	60	3	3	3	3	60
March 2012	5	5	5	100	5	5	5	5	100
1st Quarter	**11**	**11**	**8**	**73**	**8**	**8**	**8**	**8**	**73 [5]**

[1] Planned sample events based on a sampling frequency of 1 sample every 6 days. Sampling schedule used for the project is the EPA 2012 Monitoring Schedule for TSP, PB, PM-10, PM-2.5, and VOCs.
[2] Actual Sample Events includes planned sample events and any "make-up" events that were collected.
[3] Recovery rate refers to whether the $PM_{2.5}$ mass sample was valid. The project goal for $PM_{2.5}$ mass recovery rate is ≥ 80% per quarter.
[4] Data completeness refers to the validity of the entire sample as defined by valid measurements for critical elements: $PM_{2.5}$ Mass, Nitrate, Sulfate, organic carbon, and elemental carbon. Data completeness is calculated by the number of valid samples for all critical elements divided by the number of planned sample events and expressed as a percentage. Project goal for data completeness is ≥ 80% per quarter.
[5] 8 out of 11 sample events obtained valid measurements for all critical elements ($PM_{2.5}$ Mass, Nitrate, Sulfate, organic carbon, and elemental carbon). The 1/28/2012, 2/3/2012, and 2/9/2012 events had at least one critical element invalidated for the sample event.

1. INTRODUCTION

1.1 PROJECT SUMMARY

Shell Offshore Inc. (SOI) applied for an outer continental shelf (OCS) / Prevention of Significant Deterioration (PSD) air quality permit from the United States Environmental Protection Agency (EPA) in January 2010. The air quality permit is required for the operation of an oil exploratory vessel in the seas north of the Alaska coastline in the Beaufort Sea. Air quality permit R10OCS/PSD-AK-2010-01 was issued by EPA on September 19, 2011 and became effective January 27, 2012 for to SOI to operate the Noble Discoverer (Discoverer) drillship in the Beaufort Sea.

Conditions specified within the air quality permit require SOI to conduct post-construction ambient air quality and meteorological monitoring (Condition S.). The air quality permit conditions specify that $PM_{2.5}$ mass, $PM_{2.5}$ chemical speciation, horizontal wind direction and speed, temperature, solar radiation, and temperature difference measurements are to be collected.

SLR International Corp (SLR) operates ambient air and meteorological monitoring stations on behalf of SOI at Kaktovik, Alaska (Barter Island) and Point Lay, Alaska. Additionally, SLR operates an ambient air and meteorological monitoring station at Wainwright, Alaska and Deadhorse, Alaska as part of a Shell / ConocoPhillips joint monitoring venture. EPA approved the Quality Assurance Project Plans (QAPP) for Point Lay, Wainwright, and Deadhorse ambient air quality and meteorological monitoring programs on October 14, 2011. The QAPP for the Kaktovik ambient air quality and meteorological monitoring program was approved by EPA on November 16, 2011.

Permit condition S1.2 (Beaufort permit R10OCS/PSD-AK-2010-01) specifies: *"The Permittee shall use a continuous sampler and a manual sampler to measure $PM_{2.5}$. In addition, filters from the manual sampler shall be analyzed as provided for in the EPA-approved ambient air quality and meteorological plan required pursuant to Condition S.3 to allow for the chemical speciation of $PM_{2.5}$ constituents, including but not limited to sulfates, nitrates, organics, metals, sea salt, and crustal matter."*

To satisfy this permit condition, samples that are already being collected by manual samplers operated at Deadhorse were considered. However, these samplers collect samples on a single, Teflon® sample media as part of the $PM_{2.5}$ mass monitoring program. This Teflon® sample media is only appropriate for a portion of the analyses typically performed to collect $PM_{2.5}$ chemical speciation data. A supplemental sampler was installed at Deadhorse to collect $PM_{2.5}$ speciation samples to satisfy the $PM_{2.5}$ speciation monitoring requirements in the Beaufort Sea. This report summarizes speciation sample results collected at the Deadhorse station for Quarter A of the monitoring program spanning from January 1, 2012 through March 31, 2012. For more information on the Deadhorse monitoring station, refer to the Deadhorse Ambient Air Monitoring Program QAPP.

Figure 1-1. Station Location Map

Figure 1-2. Photo of monitoring station

1.2 MEASUREMENT METHODS

$PM_{2.5}$ Chemical Speciation monitoring equipment is operated using Prevention of Significant Deterioration (PSD) quality assurance practices as a guide. Samplers are installed, calibrated, and operated according to manufacturer recommended procedures. Calibration and periodic flow-rate verifications are documented throughout the monitoring program. Table 1-1 lists the parameters that are measured.

EPA STN samples are collected on a once every three day schedule all year-round to assess national trends in background pollutant concentrations. Higher frequency sampling schedule is generally followed by locations where $PM_{2.5}$ concentrations tend to be relatively high, pose a health concern, or the area is of interest to assess national trends. Because observed $PM_{2.5}$ mass concentrations along the Beaufort Sea have historically been very low, and the cost and logistical difficulties of operating a sample collection program in remote Alaska, the project adopted a one sample every six day frequency and schedule.

A $PM_{2.5}$ chemical speciation sampler supplements existing ambient air quality and meteorological monitoring equipment already in operation at the representative location. Met One SuperSASS™ samplers capable of collecting samples on multiple sample media (Teflon, Nylasorb, and quartz) are used to ensure proper sample collection and handling. Met One SuperSASS™ samplers were selected after careful consideration of site characteristics and after consideration of site operator survey results provided in *Evaluation of $PM_{2.5}$ Chemical Speciation Samplers for Use in the EPA National $PM_{2.5}$ Chemical Speciation Network*, Table II-15 (EPA-454-R-01-005). Critical sampler characteristics include single person field installation ability, quick installation time, sampler ease of use for both sample collection and audit and calibration, and sampler operation reliability. SuperSASS™ samplers are currently used in the EPA STN sampling network in combination with another sampler specific to carbon sample collection.

Table 1-1. Chemical Speciation Parameters

Parameter / Species	Symbol	Analysis Method	AQS Parameter
Mass	$PM_{2.5}$	Gravimetry	88502
Sulfate	$SO_4^=$	Ion Chromatography[1]	88403
Nitrate	NO_3^-	Ion Chromatography[1]	88306/88310
Chloride	Cl^-	Ion Chromatography[1]	88203
Ammonium	NH_4^+	Ion Chromatography[1]	88301
Potassium	K^+	Ion Chromatography[1]	88303
Sodium	Na^+	Ion Chromatography[1]	88302
Organic Carbon (TOR)	OCR	Thermal/Optical Reflectance[2]	88370
Organic Carbon (TOT)	OCT	Thermal/Optical Transmission[2]	88355
OC-Peak 1	OC1	Thermal/Optical Reflectance[2]	88374
OC-Peak 2	OC2	Thermal/Optical Reflectance[2]	88375
OC-Peak 3	OC3	Thermal/Optical Reflectance[2]	88376
OC-Peak 4	OC4	Thermal/Optical Reflectance[2]	88377
Pyrolized Carbon (TOR)	OPR	Thermal/Optical Reflectance[2]	88378
Pyrolized Carbon (TOT)	OPT	Thermal/Optical Transmission[2]	88388
Elemental Carbon (TOR)	ECR	Thermal/Optical Reflectance[2]	88380
Elemental Carbon (TOT)	ECT	Thermal/Optical Transmission[2]	88357
EC-Peak 1	EC1	Thermal/Optical Reflectance[2]	88383
EC-Peak 2	EC2	Thermal/Optical Reflectance[2]	88384
EC-Peak 3	EC3	Thermal/Optical Reflectance[2]	88385
Total Carbon	TC	Thermal/Optical Reflectance[2]	88312

[1] Analytical measurement determined by NIOSH 7903 / EPA 300.0 Ion chromatography method
[2] Analytical measurement determined by IMPROVE-A carbon analysis method.

Table 1-2. Chemical Speciation Parameters

Element [1]	Symbol	Element [1]	Symbol
Sodium	Na	Germanium	Ge
Magnesium	Mg	Arsenic	As
Aluminum	Al	Selenium	Se
Silicon	Si	Bromine	Br
Phosphorous	P	Rubidium	Rb
Sulfur	S	Strontium	Sr
Chlorine	Cl	Yttrium	Y
Potassium	K	Zirconium	Zr
Calcium	Ca	Molybdenum	Mo
Titanium	Ti	Palladium	Pd
Vanadium	V	Silver	Ag
Chromium	Cr	Cadmium	Cd
Manganese	Mn	Indium	In
Iron	Fe	Tin	Sn
Cobalt	Co	Antimony	Sb
Cerium	Ce	Cesium	Cs
Nickel	Ni	Barium	Ba
Copper	Cu	Lanthanum	La
Zinc	Zn	Mercury	Hg
Gallium	Ga	Lead	Pb

[1] Analytical measurement determined by X-ray Fluorescence Analysis (XRF) EPA Method IO-3.3

Table 1-3. Summary of MQOs for the $PM_{2.5}$ Chemical Speciation Monitoring Program

Quality Objective	Assessment Method	Acceptance Criteria[1]	Corrective Actions
Accuracy	Sampler Flow Verifications	± 10%	Re-calibrate sampler flow
	Laboratory Quality Control Samples	Gravimetric / Mass - ± 5 µg X-ray Fluorescence (XRF) / Elements - ± 10% Ion Chromatography (IC) / Ions - ± 10% Elemental / Total Carbon (TOR / TOT) - ± 10%	Re-calibrate, re-analyze QC and field samples
Precision[2]	Laboratory Replicates	Gravimetric / Mass - ± 5 µg X-ray Fluorescence (XRF) / Elements - ± 7% or 5% Ion Chromatography (IC) / Ions - ± 10% Elemental Carbon (TOR / TOT) - ± 10% Total Carbon (TOR / TOT) - ± 10%	Re-calibrate, re-analyze QC and field samples
Data Completeness	Calculated	≥ 80% per monitoring quarter (valid samples defined by combined $PM_{2.5}$, Sulfate, OC, EC, Nitrate valid measurements for the sampling event)	Collect additional samples; Re-analysis of samples by laboratory
Representativeness	Sampler siting	Meets $PM_{2.5}$ requirements	N/A
Detectability[3]	Laboratory determined detection limits	Gravimetric / Mass – 0.3 µg/m^3 X-ray Fluorescence (XRF) / Elements – 0.05 – 20 ng/m^3 Ion Chromatography (IC) / Ions - 10 – 100 ng/m^3 Elemental Carbon (TOR / TOT) - 100 ng/m^3 Total Carbon (TOR / TOT) - 250 ng/m^3	N/A
Comparability	Analytical methodology	Analytical laboratory experienced with STN/IMPROVE Measurement methods consistent with STN/IMPROVE	N/A

[1] Laboratory acceptance criteria defined from IMPROVE MQO goals. *Interagency Monitoring of Protected Visual Environments, Quality Assurance Plan OAQPS Category 1 QAPP*. Revision 0.0 March 2002. Section 4.6 Measurement Quality Objectives.
[2] Precision objectives for measurements that are significantly above instrument detection limits. Assessment of measurements near or below detection limits exaggerates statistical uncertainty. XRF precision criteria depends upon the number of fluorescers for a particular element.
[3] Detection limits vary for each analytical parameter.

1.3 VARIATIONS FROM THE QUALITY ASSURANCE PROJECT PLAN

Table 1-3 summarizes variations from the Quality Assurance Project Plan during the monitoring period.

Table 1-3 QAPP Variation Table

Item / Procedure	Summary of QAPP Variation	Reason for making the variation
During the monitoring period, there were no variations from the approved procedures and criteria specified in the Discoverer $PM_{2.5}$ Speciation Monitoring Program Quality Assurance Project Plan (QAPP).		

2. STATION PERFORMANCE SUMMARY

2.1 SIGNIFICANT PROJECT EVENTS

Table 2-1 summarizes the significant events that occurred at the Deadhorse $PM_{2.5}$ Speciation monitoring station between January 1, 2012 and March 31, 2012.

Table 2-1. Chronology of Significant Events

Date	Event
January 27, 2012	Installation of samplers and initial calibration.
January 28, 2012	First scheduled sampling event. Sampler operated but suspect due to incorrect pump solenoid installation by manufacturer. Filters were analyzed by the lab but were invalidated due to inconsistency of measurements with other collocated PM sampler results for the same time period.
February 3, 2012	Low sampler flow and volume due to incorrect pump solenoid installation by sampler manufacturer. Sample was analyzed by the lab but was invalidated due to insufficient sample volumes collected.
February 9, 2012	Low sampler flow and volume due to incorrect pump solenoid installation by sampler manufacturer. Sample was analyzed by the lab but was invalidated due to insufficient sample volumes collected.
February 10, 2012	Pump solenoid was replaced.
February 11, 2012	Monthly QC verification and quarterly calibration, all QC checks met acceptance criteria.
March 5, 2012	Monthly QC verification, all QC checks met acceptance criteria.
March 6, 2012	Performance audit conducted.
March 7, 2012	Make up for missed 3/4/2012 scheduled sampling event.
March 13, 2012	Make up for missed 3/10/2012 scheduled sampling event.

2.2 MISSING, INVALID, AND ADJUSTED DATA

Table 2-2 provides a summary of the recovery and data completeness during the period. While no regulatory-mandated data completeness requirement exists, the project has set a data completeness goal of 80 percent per calendar quarter. The information provided below includes summary statistics that may also include make-up sampling events (itemized in Table 2-1) that were missed to due logistical difficulties or sampler malfunction. An explanation of significant events causing data to be invalidated is discussed below.

The January 28, February 3, and February 9, 2012 events had at least one critical element invalidated for the sample event and as a result the project only achieved 73 percent data completeness for the quarter. Only 8 out of 11 possible sample events obtained valid measurements for all critical elements ($PM_{2.5}$ Mass, Nitrate, Sulfate, organic carbon, and elemental carbon). The January 28, February 3, and February 9, 2012 sampling events were invalidated due to sampler malfunctions.

Table 2-2. Data Recovery and Data Completeness Summary

Period	Planned Sample Events [1]	Actual Sample Events [2]	Valid $PM_{2.5}$ Mass Samples	Recovery Rate (%) [3]	Valid Nitrate (NO_3) Samples	Valid Sulfate (SO_4) Samples	Valid Organic Carbon (OC) Samples	Valid Elemental Carbon (EC) Samples	Data Completeness (%) [4]
January 2012	1	1	0	0	0	0	0	0	0
February 2012	5	5	3	60	3	3	3	3	60
March 2012	5	5	5	100	5	5	5	5	100
1st Quarter	**11**	**11**	**8**	**73**	**8**	**8**	**8**	**8**	**73**

[1] Planned sample events based on a sampling frequency of 1 sample every 6 days. Sampling schedule used for the project is the EPA 2012 Monitoring Schedule for TSP, PB, PM-10, PM-2.5, and VOCs.
[2] Actual Sample Events includes planned sample events and any "make-up" events that were collected.
[3] Recovery rate refers to whether the $PM_{2.5}$ mass sample was valid. The project goal for $PM_{2.5}$ mass recovery rate is ≥ 80% per quarter.
[4] Data Completeness refers to the validity of the entire sample as defined by valid measurements for critical elements: $PM_{2.5}$ Mass, Nitrate, Sulfate, organic carbon, and elemental carbon. Data completeness is calculated by the number of valid samples for all critical elements divided by the number of planned sample events and expressed as a percentage. Project goal for data completeness is ≥ 80% per quarter.

Table 2-3. Data Recovery and Data Completeness Details

EPA Scheduled Sample Date	Actual Sample Date	Teflon Filter		Nylon Filter		Quartz Filter		Complete	Comments
		$PM_{2.5}$	XRF Elements	Sulfate	Nitrate	Elemental Carbon	Organic Carbon		
1/28/12	1/28/12	*Invalid*	*Invalid*	*Invalid*	*Invalid*	*Invalid*	*Invalid*	**No**	
2/3/12	2/3/12	*Invalid*	*Invalid*	*Invalid*	*Invalid*	*Invalid*	*Invalid*	**No**	
2/9/12	2/9/12	*Invalid*	*Invalid*	*Invalid*	*Invalid*	*Invalid*	*Invalid*	**No**	
2/15/12	2/15/12	Valid	Valid	Valid	Valid	Valid	Valid	Yes	
2/21/12	2/21/12	Valid	Valid	Valid	Valid	Valid	Valid	Yes	
2/27/12	2/27/12	Valid	Valid	Valid	Valid	Valid	Valid	Yes	
3/4/12	3/7/12	Valid	Valid	Valid	Valid	Valid	Valid	Yes	Makeup Run
3/10/12	3/13/12	Valid	Valid	Valid	Valid	Valid	Valid	Yes	Makeup Run
3/16/12	3/16/12	Valid	Valid	Valid	Valid	Valid	Valid	Yes	
3/22/12	3/22/12	Valid	Valid	Valid	Valid	Valid	Valid	Yes	
3/28/12	3/28/12	Valid	Valid	Valid	Valid	Valid	Valid	Yes	
Number Runs		**11**	**11**	**11**	**11**	**11**	**11**	**11**	
Valid Runs		**8**	**8**	**8**	**8**	**8**	**8**	**8**	
Recovery		**73%**	**73%**	**73%**	**73%**	**73%**	**73%**		
Completeness								**73%**	

2.3 INSTRUMENT CALIBRATION

Sampler calibration verifications were performed on the dates specified in Table 2-1. Calibration summary reports are included in Appendix B.

2.4 INDEPENDENT QUALITY ASSURANCE AUDITS

Performance audit of the sampler was conducted on March 6, 2012. Audit findings indicated that the sampler was operating within acceptable criteria. Complete audit reports are included in Appendix B.

3. DATA

Permit condition S1.2 lists the desired chemical speciation of $PM_{2.5}$ constituents as: *"including but not limited to sulfates, nitrates, organics, metals, sea salt, and crustal matter".* To satisfy this permit condition, some interpretation of the definition of each constituent listed in the permit was required. *Sulfates* and *nitrates* analysis was performed by ion chromatography which provides a comprehensive assessment of inorganic sulfate and nitrate salts. Organic carbon measurements were obtained to assess *organic* content of the $PM_{2.5}$ samples. XRF analysis for the parameters listed in Table 1-2 was defined to collectively satisfy the permit condition for *metals* analysis. The combination of alkali metals (sodium, potassium), alkaline earth metals (magnesium, calcium), and anions (chloride, bromine, nitrate, sulfate) were collectively measured as *sea salt*. The requirement to measure *crustal matter* was satisfied by total and elemental carbon as well as from $PM_{2.5}$ total mass measurements.

Given the large number of parameters measured by the project, certain critical parameters ($PM_{2.5}$ Mass, Sulfate, Nitrate, Elemental Carbon and Organic Carbon) were selected for more involved analysis and presentation. These parameters, as described in section 2.2 provide the basis for overall project data quality objective assessment. Figures 3-1 through 3-4 provide plots of the daily 24-hour average concentrations for these primary $PM_{2.5}$ chemical speciation parameters of concern. Plots for the remaining parameters are not included in this report, however data is provided in the accompanying project data spreadsheet.

A general trend in the data was observed where the accumulative concentrations of the individual parameters exceeded the $PM_{2.5}$ total mass measurement. Theoretically the accumulated concentrations of all the parameters should be less than or equal to the total mass measurement. After careful review of the data, it was concluded that the uncertainties of each measurement, particularly at such low ambient concentrations, contributed to this observation.

The field blank from Wainwright dated March 10, 2012 contained a higher-than-expected level of $PM_{2.5}$ mass however was within the project-specified acceptance a level (<30 µg) for a field blank. Although this sample was sent to Wainwright, it was shipped with samples from Deadhorse and the results could indicate a possible sample handling compromise. A careful examination of the data from samples collected at Deadhorse suggests that none of the Deadhorse samples were compromised. Additionally, results for pyrolized carbon indicated a relatively high negative result. The sample was re-analyzed at the laboratory and confirmed. The high negative result was due to inherent measurement variability and the results exaggerated due to the multiplicative effect to convert the laboratory analytical results to the final reporting units.

Unless described in section 2.2 Missing, Invalid, or Adjusted Data, all data collected for the project were determined to meet project quality assurance objectives.

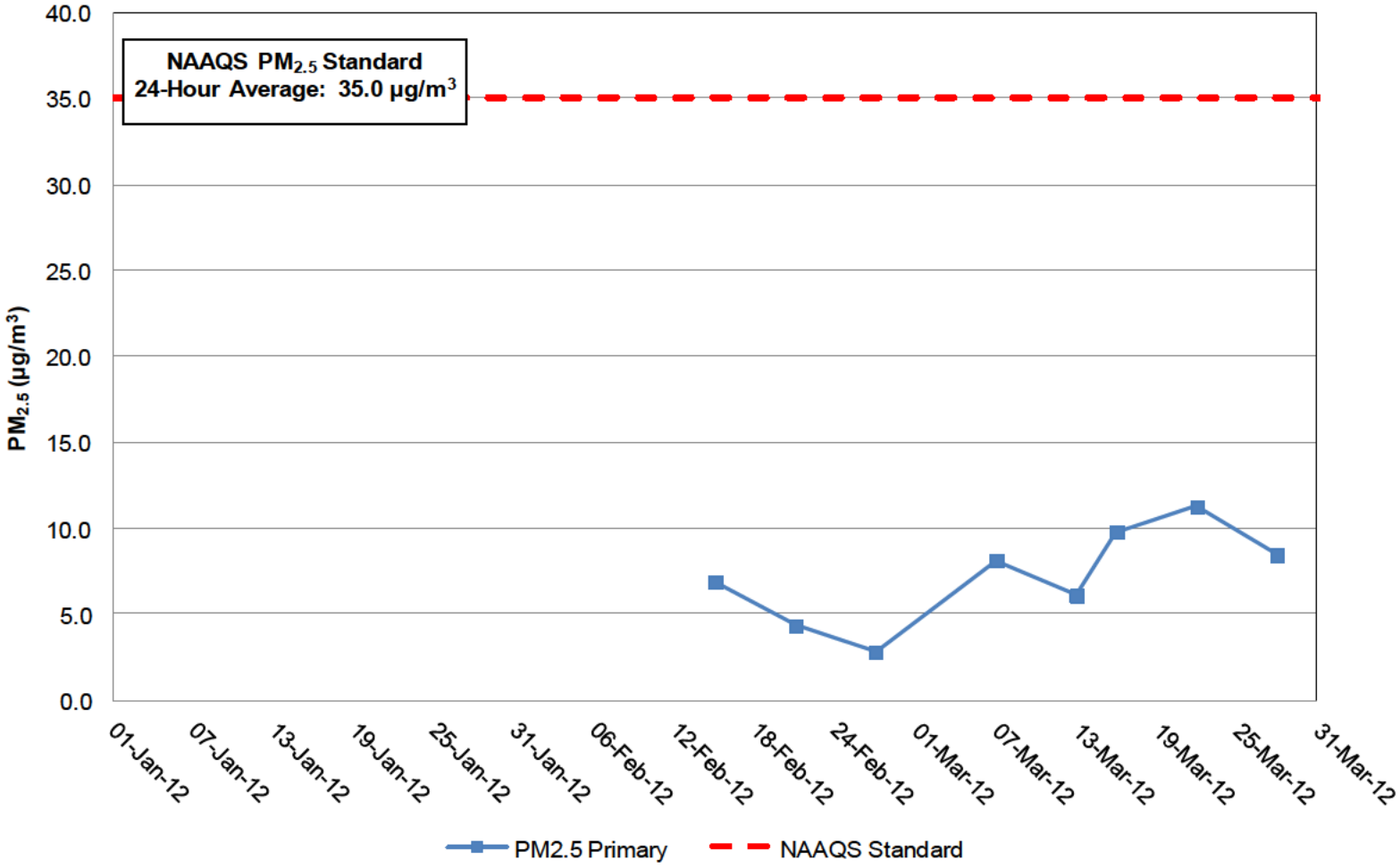

Figure 3-1. 24-hour Average $PM_{2.5}$ Mass and NAAQS Standard

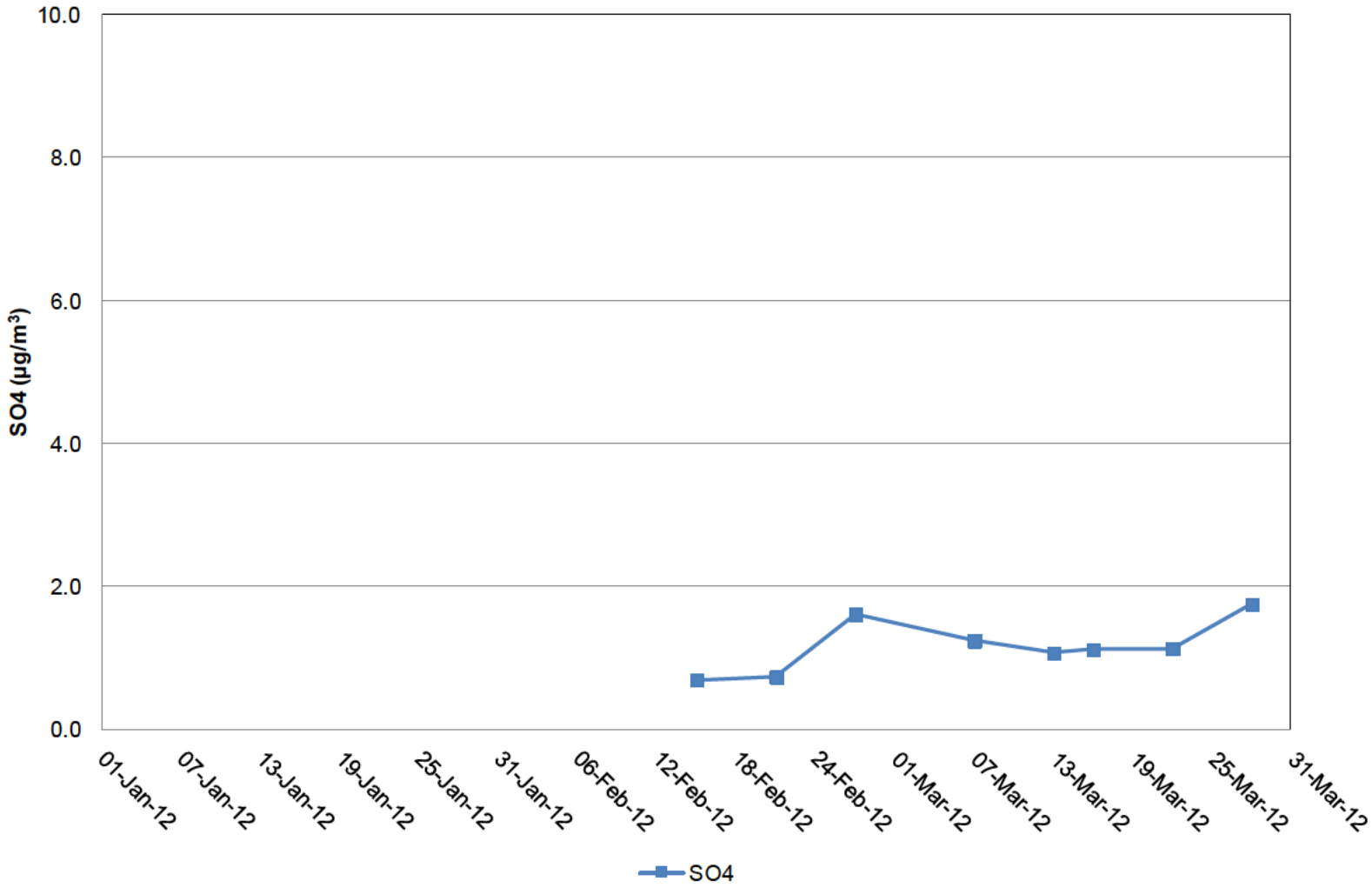

Figure 3-2. 24-hour Average Sulfate Concentration

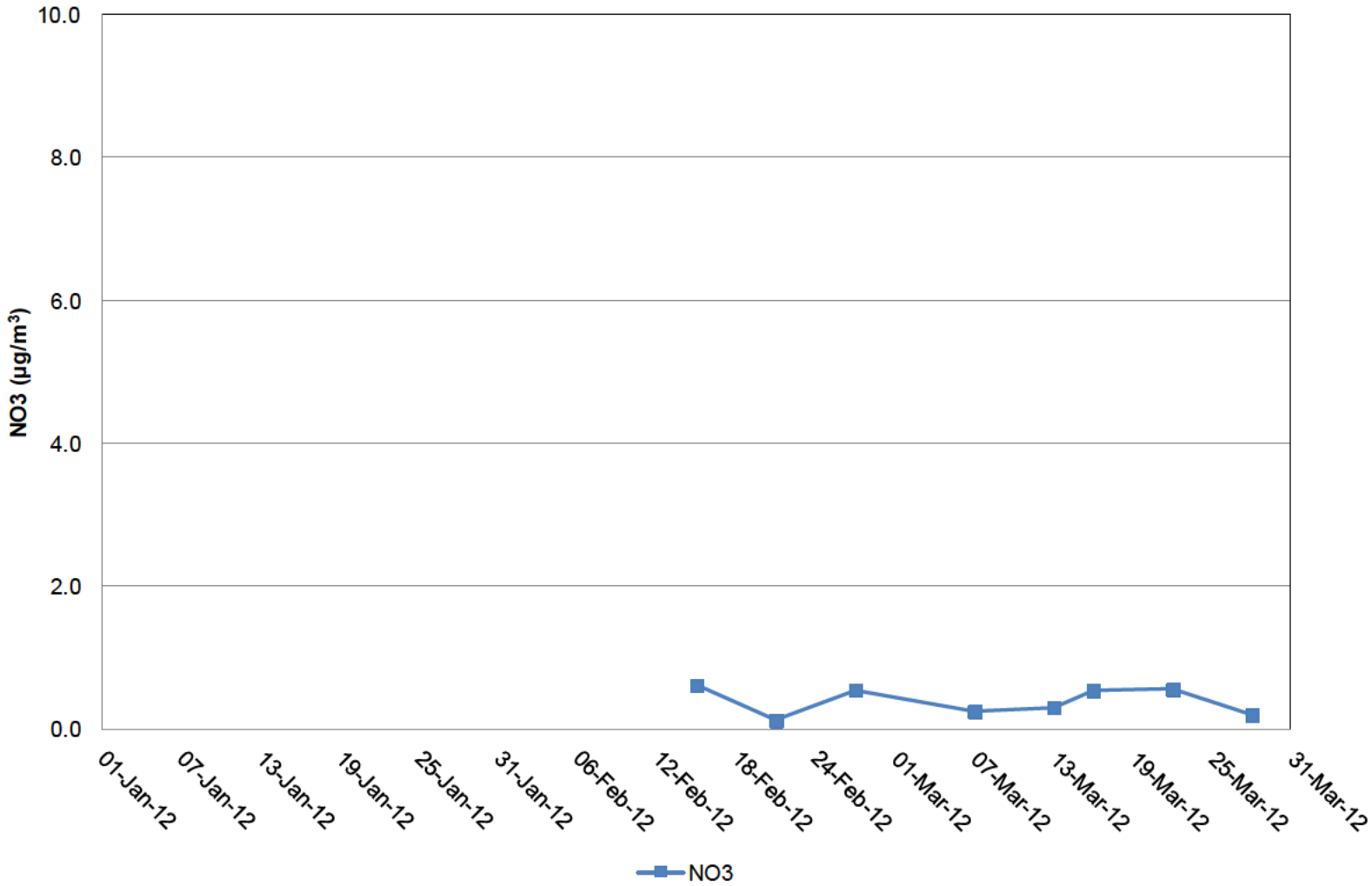

Figure 3-3. 24-hour Average Nitrate Concentration

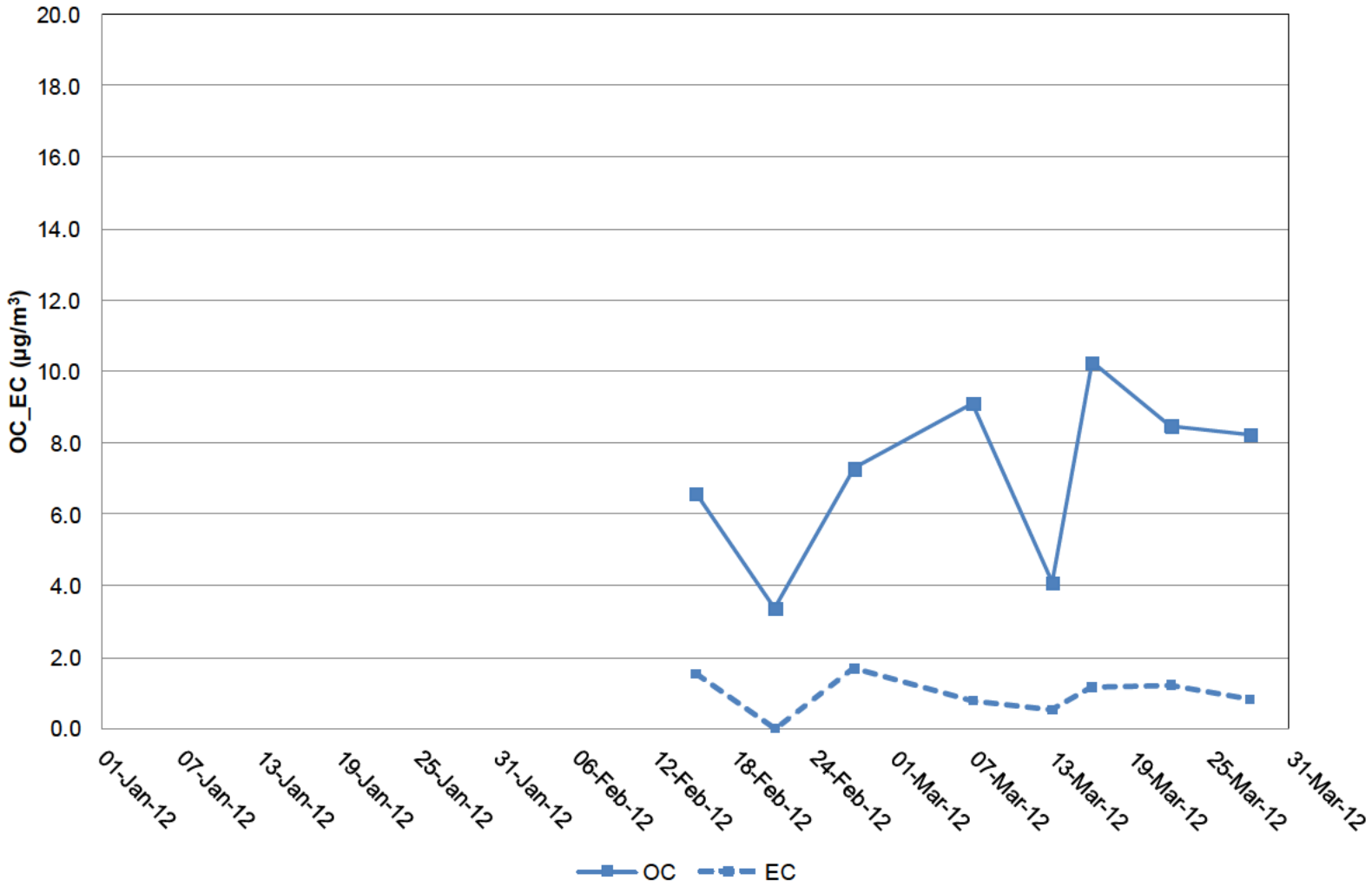

Figure 3-4. 24-hour Average Elemental and Organic Carbon Concentrations

4. REFERENCES

Guidance for Data Quality Assessments: Practical Methods for Data Analysis (EPA QA/G-9).

Guidelines on the Meaning and the Use of Precision and Bias Data Required by 40 CFR Part 58 Appendix A (EPA-454/B-07-001, January 2007).

Meteorological Monitoring Guidance for Regulatory Modeling Applications, (EPA-454/R-99-005, February 2000).

PSD Quality Ambient Air Quality & Meteorological Monitoring Annual Data Report Format (ADEC,
October 2006)

Quality Assurance Project Plan for the Deadhorse Ambient Air Monitoring Program (SLR Version 2.0 November 2011)

Quality Assurance Project Plan Addendum for the Discoverer $PM_{2.5}$ Speciation Monitoring Program (SLR Version 2.0, April 2012)